

Chiral Induction in the Ionothermal Synthesis of a 3D Chiral Heterometallic Metal–Organic Framework Constructed from Achiral 1,4-Naphthalenedicarboxylate

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Supporting Information

ABSTRACT: A chiral heterometallic compound, [(EMIM)NaCu(1,4-ndc)₂]_n (**1**), constructed from the achiral 1,4-naphthalenedicarboxylate (1,4-ndc) ligand has been ionothermally synthesized and structurally and magnetically characterized. The chiral induction effect of the enantiopure 1-ethyl-3-methylimidazolium (EMIM) *L*-lactate additive in the ionothermal reaction is briefly discussed.

Chiral solids are of interest and great importance because these materials have potential applications in enantioselective separations, heterogeneous asymmetric syntheses, nonlinear optics, and magnetism.¹ Recently developed metal–organic framework (MOF) materials or coordination polymers containing both inorganic and organic units within the frameworks have shown great promise for the preparation of chiral materials.² The general approach to a chiral compound is using a chiral molecule as the primary linker or as a auxiliary ligand, which is the most effective method for the synthesis of chiral compounds.³ However, because of the limitation of the chiral pool and very often the high cost of chiral ligands, it is highly desirable to create chiral compounds from achiral precursors. A chiral compound obtained from totally achiral starting precursors without a chiral source via spontaneous resolution is also known.⁴ It is worth pointing out that such a spontaneous resolution process is not controllable from run to run. Recently, a new approach called chiral induction, pioneered by Morris and Bu,⁵ was developed for the synthetic design of chiral framework materials wherein chirality is induced in the final product through a chiral solvent or a chiral additive that is not incorporated into the final product. Morris' group demonstrates the induction of chiral nickel benzene-1,3,5-tricarboxylate frameworks using a 1-butyl-3-methylimidazolium *D*- or *L*-aspartate ionic liquid solvent.⁶ The chiral *D*- or *L*-aspartate anion of the ionic liquid is not occluded by the final chiral solids. Different from induction of the chiral solvent, induction by chiral additives occurs in a predominantly achiral solvent environment. To achieve effective chiral induction, there should be relatively strong interactions between chiral additives and achiral frame-

work building blocks. A notable example of chiral induction involving the use of chiral (–)-cinchonidine or (+)-cinchonine additives to induce chiral indium thiophene-2,5-dicarboxylate frameworks is reported by Bu's group.⁷ On the basis of their examples, Bu et al. think that chiral induction is likely to involve chemical bonding interactions between metal sites of the framework and a chiral additive. Furthermore, they proposed that a chiral additive bearing chemistry similar to that of the framework building unit is needed,^{5a} which satisfies the need for the formation of ultimate chiral frameworks effectively. We have followed this approach for synthesis of the chiral compound with an achiral 1,4-naphthalenedicarboxylate (1,4-ndc) ligand induced by a chiral additive under ionothermal conditions. In the present work, the chiral additive is 1-ethyl-3-methylimidazolium *L*-lactate (EMIM-*L*-lactate). The chiral *L*-lactate portion of the liquid has bonding features similar to those of the framework building unit of the 1,4-ndc ligand. Herein we report the ionothermal synthesis, crystal structure, and magnetic properties of a chiral MOF of [(EMIM)NaCu(1,4-ndc)₂]_n (**1**). To the best of our knowledge, no heterometallic Cu^{II}-1,4-ndc compound has been reported previously.

Ionothermal reaction of Cu(NO₃)₂, 1,4-naphthalenedicarboxylic acid (1,4-H₂ndc), and EMIM-*L*-lactate in a 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) solvent afforded blue crystals of **1** (Figure 1).⁸ Its IR spectrum exhibits

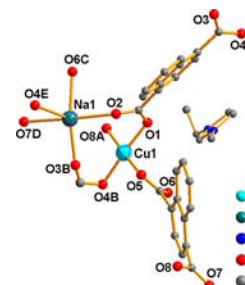


Figure 1. Coordination environments of the metal centers in **1**.

Received: April 10, 2013

Published: June 3, 2013

sharp peaks centered at 1601, 1400, and 1363 cm^{-1} , which are the expected absorptions for stretching vibrations of the carboxylate groups. The powder X-ray diffraction (PXRD) pattern is in good agreement with the ones simulated from single-crystal structural data, which confirmed the purity of the bulk sample (Figure S1 in the Supporting Information, SI). Single-crystal X-ray diffraction analyses showed that **1** crystallizes in the chiral $P4_1$ space group (Table S1 in the SI).⁹ The solid-state circular dichroism (CD) spectra for samples obtained from two separate synthetic batches further confirmed the homochirality or enantioenrichment of the bulk material of **1** (Figure S2 in the SI). Compound **1** features an anionic three-dimensional (3D) framework charged with extraframework imidazolium cations. The asymmetric unit of **1** consists of one Cu^{II} ion, one Na^{I} ion, two $1,4\text{-ndc}^{2-}$ dianions, and one $[\text{EMIM}]^+$ cation. It should be noted that the Na ion derives from the EMIM- BF_4 ionic liquid, which contains a small amount of Na^{I} impurity. As depicted in Figure 1, the Cu ion is four-coordinated by four carboxylate O atoms from four individual $1,4\text{-ndc}^{2-}$ ligands in a distorted square-planar geometry, with the Cu–O bond lengths varying from 1.929(3) to 1.984(3) Å (Table S2 in the SI). The Na ion has a square-pyramidal $[\text{NaO}_5]$ coordination geometry with a O4E atom at the capped position (Figure 1); all five coordination sites are filled by carboxylate O atoms from five $1,4\text{-ndc}^{2-}$ ligands. The Na–O bond lengths range from 2.305(4) to 2.598(5) Å. Two crystallographically independent $1,4\text{-ndc}^{2-}$ ligands exhibit two different coordination modes. One serves as a pentadentate ligand bridging three Na and two Cu ions through its three unidentate carboxylate O atoms and one η^2 -carboxylate O atom (Scheme S1 in the SI). The other displays a tetradentate coordination mode using its four unidentate carboxylate O atoms bridging two Na and two Cu ions.

As depicted in Figure 2, the carboxylate groups bridge Cu^{II} and Na^{I} ions alternately into an infinite right-handed helical chain

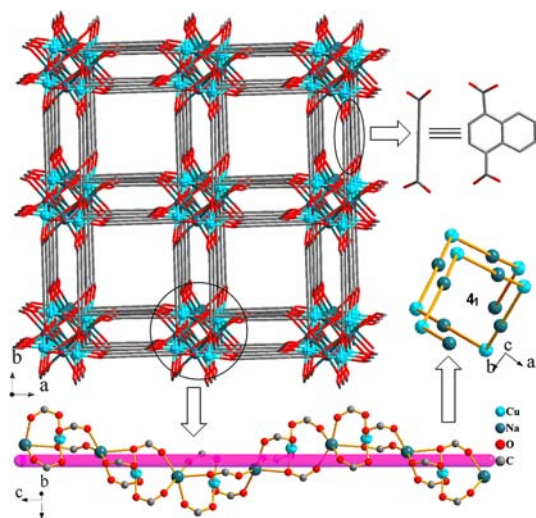


Figure 2. 3D $[\text{NaCu}(1,4\text{-ndc})_2]^{n-}$ framework of **1** showing the right-handed helical chain and 4_1 helix.

running along the c axis. The pitch length of the helical chain is 24 Å, which is identical with the c -axis length. The helix is generated around the crystallographic 4_1 screw axis (Figure 2), which is consistent with the compound crystallizing in the $P4_1$ space group. Each helical chain serves as a secondary building unit and is further linked to its four adjacent neighbors with the same handedness in two orthogonal directions through naphthalene

links, generating a homochiral 3D $[\text{NaCu}(1,4\text{-ndc})_2]^{n-}$ anionic framework, as shown in Figures 2 and 3. The chirality in structure

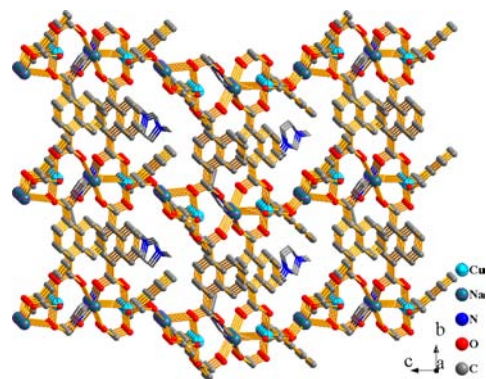


Figure 3. 3D framework of **1** (view along the a axis). The imidazolium $[\text{EMIM}]^+$ cations are situated in the 1D channels.

1 is a result of the 4_1 axis in the symmetry. Therefore, the chirality in the present compound is derived from the presence of helices. The 3D framework has one-dimensional (1D) channels along the a and b axes (Figures 3 and S3). As shown in Figure S4 in the SI, each Cu center is linked by four $1,4\text{-ndc}^{2-}$ ligands in orthogonal directions into a (4,4) layer, and the resulting parallel (4,4) layers are pillared by the Na^{I} centers through Na–O bonds. Thus, the whole framework can be topologically represented as a pcu net. The imidazolium $[\text{EMIM}]^+$ cations of the ionic liquids act as extraframework charge-balancing species for the $[\text{NaCu}(1,4\text{-ndc})_2]^{n-}$ anionic framework. The $[\text{EMIM}]^+$ cations are situated in the 1D open channels and π -interact with the benzene component of the $1,4\text{-ndc}^{2-}$ ligands of the host framework with a center-to-center separation of 3.71 Å. Thus, the $[\text{EMIM}]^+$ cation not only adopts a charge-compensating role but also acts as a space filler in the material. We have been unable to remove it without causing the structure to collapse (Figure S5 in the SI).

A synthetic strategy for chiral compounds induced by chiral additives from achiral precursors provides more opportunities for the development of novel chiral solids. However, there are only a few examples of chiral induction reported to date.^{5–7,10} Two different induction effects of the chiral additive can be classified. One is, with the chiral additive, a homochiral (or enantioenriched) bulk sample can be produced, while the absence of a chiral additive would produce the same chiral crystals in a racemic conglomerate. In this case, the role of the chiral additive is to create an enantiomeric bias to favor one chiral form of the same crystal structure. The other is the crystallization process can give totally different crystal structures depending on whether chiral additives are present or not. In this case, the chiral additive not only controls the enantiomeric excess but also contributes to the formation of a given crystalline phase. In the present case, the reaction of $\text{Cu}(\text{NO}_3)_2$ and $1,4\text{-H}_2\text{ndc}$ in the presence of a chiral EMIM-L-lactate additive under ionothermal conditions leads to chiral compound **1**. Attempts to obtain the compound with the opposite handedness of **1** induced by the chiral EMIM-D-lactate additive with varying diverse reaction conditions are not successful. Moreover, in the absence of EMIM-L-lactate and EMIM-D-lactate under similar reactions, no product can be produced. These results indicate that the EMIM-L-lactate additive not only has a chiral induction role in crystallization of compound **1** but also contributes to the formation of the present crystalline phase. For an effective chiral induction, the chiral

information from a chiral species to the nucleus or growing crystallite needs to be very specific. Thus, the interactions between the chiral species and the substrate crystals probably need to be quite strong. Recent examples of chiral induction by additives demonstrated by Morris and Bu groups suggest that chemical bonding interactions between the chiral additives and metal centers might be responsible.⁵ In this case, the EMIM-L-lactate additive has three donor atoms: two carboxylate O atoms and one hydroxyl O atom. The hydroxyl O atom is directly bonded to the asymmetric C atom. Thus, the most likely interaction is the formation of the five-membered ring through chelation of the hydroxyl O atom and one of the carboxylate O atoms to the metal site.

Variable-temperature magnetic measurements were performed on a polycrystalline sample of **1** in the temperature range of 2–300 K in an applied magnetic field of 2 kOe. The plots of $\chi_M T$ versus T together with $1/\chi_M$ versus T , where χ_M is the molar magnetic susceptibility per Cu unit, are shown in Figure 4.

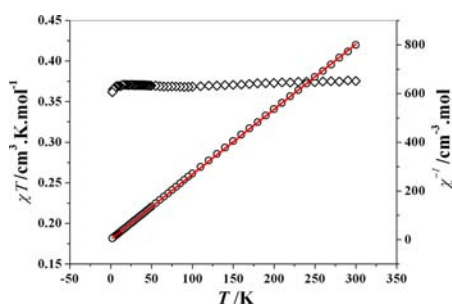


Figure 4. Plots of $\chi_M T$ and $1/\chi_M$ versus T for **1**. The solid line represents the best theoretical fit.

The $\chi_M T$ value at room temperature is $0.374 \text{ cm}^3 \text{ K mol}^{-1}$, which is in good agreement with the value of $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ for the uncoupled $S = 1/2$ spin of the Cu^{II} ion (assuming $g_{\text{Cu}^{\text{II}}} = 2.0$). As the temperature decreases, the $\chi_M T$ product gradually decreases to reach a flat in the temperature range of 110–10 K due to the isolated Cu ions and then drops to a minimum of $0.36 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The magnetic susceptibility data between 300 and 2 K obey the Curie–Weiss law $1/\chi_M = (T - \theta)/C$, giving the Curie constant C of $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ and the Weiss constant θ of -0.61 K . The small negative Weiss constant is indicative of weak antiferromagnetic interactions. The crystal structure shows that **1** is a 3D network formed from 1,4-ndc²⁻ linking of the 1D carboxylate-bridged heterometallic helical chains. Thus, the magnetic interaction between helical chains is very weak because there is no available bridge for mediating the coupling interaction. In the 1D helix, the Cu^{II} and Na^{I} ions are alternately arranged with the shortest $\text{Cu}\cdots\text{Cu}$ separation of 6.61 \AA (Figure 2), which is a somewhat long separation for the magnetic coupling Cu^{II} ions. Therefore, only a weak antiferromagnetic interaction is expected.

In summary, induction of chiral **1** by a chiral EMIM-L-lactate additive under ionothermal conditions is presented. The induction of chiral materials from achiral precursors with a chiral source opens up new opportunities in the preparation of chiral materials.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, summary of crystal data and structural refinements, table of bond lengths and angles, X-ray crystallo-

graphic files in CIF format, CD spectra, 3D structure, TGA curve, and PXRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the NNSF of China (Grants 20901033 and 21101081), the Scientific Research Foundation for the Returned Overseas Chinese Scholars (SEM), the NSF of Jiangxi (Grants 20122BAB203004 and 201322BAB203001), and a project of the Education Department of Jiangxi (Grant GJJ13242).

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- (8) Synthesis of **1**: A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (48.3 mg, 0.2 mmol), 1,4- H_2ndc (86.5 mg, 0.4 mmol), and EMIM-L-lactate (100 mg, 5 mmol) was placed in a 25 mL Parr Teflon-lined stainless steel vessel and mixed with 500 mg of EMIM-BF₄. The vessel was sealed and heated to 140 °C. This temperature was kept for 5 days, and then the mixture was naturally cooled to room temperature to form blue crystals of **1** [yield: 0.076 g, 61% based on $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$].
- (9) Crystal data: $\text{C}_{30}\text{H}_{23}\text{N}_2\text{O}_8\text{CuNa}$, $M_r = 626.03$, tetragonal, space group $P4_1$, $a = 10.6642(10) \text{ \AA}$, $b = 10.6642(10) \text{ \AA}$, $c = 23.998(5) \text{ \AA}$, $V = 2729.2(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.524 \text{ mg/m}^3$, $\mu = 0.873 \text{ mm}^{-1}$, $R1 = 0.0375$, $wR2 = 0.0749$ [$I > 2\sigma(I)$], Flack parameter 0.004(15).
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